DETAILED STUDY ON MEMBRANE DISTILLATION:

SCALING AND FOULING CONTROL

by

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Doctoral of Philosophy

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CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I certify that this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledge within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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"Your legs will get heavy and tired. Then comes a moment of feeling the wings you've grown, lifting ~ Rumi"

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*Articles related to the thesis.

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6. *Jeong, S., **Naidu, G**., Vigneswaran, S. Submerged membrane adsorption bioreactor as a pretreatment in seawater desalination for biofouling control. The 5th CESE Conference. 9 - 13 September 2012, Melbourne, Australia.
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LIST OF ABBREVIATIONS

AA	: Alginic acid
AGMD	: Air gap membrane distillation
AOC	: Assimilable organic carbon
ATP	: Adenosine tri-phosphate
BB	: Building blocks
BSA	: Bovine serum albumin
CF	: Concentration factor
CFU	: Colony forming unit
CP	: Concentration polarisation
CSD	: Crystal size distribution
DCMD	: Direct contact membrane distillation
DI	: Deionized
DOC	: Dissolved organic carbon
EBCT	: Empty bed contact time
EDS	: Energy dispersion spectrometry
FE-SEM	: Field emission scanning electron microscope
GAC	: Granular activated carbon
GE	: General Electrics
GOR	: Gain output ratio
HA	: Humic acid
HMW	: High molecular weight
HRT	: Hydraulic retention time
HS	: Humic substances
IC	: Ion chromatography
ICP	: Inductively coupled plasma
LC-OCD	: Liquid chromatography-organic carbon detection
LMW	: Low molecular weight
MD	: Membrane distillation
MF	: Microfiltration
MO	: Mixed organic
MP-AES	: Microwave plasma atomic emission spectrometer
MW	: Molecular weight

NF	: Nanofiltration
NOM	: Natural organic matter
PAC	: Powder activated carbon
PP	: Permeate production
PTFE	: Polytetrafluoroethylene
RO	: Reverse osmosis
RR	: Recovery ratio
SGMD	: Sweeping gas membrane distillation
SMABR	: Submerged membrane adsorption bioreactor
SR	: Saturation ratio
SW	: Seawater
SWRO	: Seawater reverse osmosis
TDC	: Total direct cell count
TDS	: Total dissolved solids
TP	: Temperature polarisation
TSS	: Total suspended solids
UF	: Ultrafiltration
UF-MFI	: Ultrafiltration-modified fouling index
UV	: Ultraviolet
VCF	: Volume concentration factor
VMD	: Vacuum membrane distillation
V-MEMD	: Vacuum multi effect membrane distillation
VR	: Vapour transport resistance

LIST OF SYMBOLS

$_b$	: bulk
$_f$	: feed
$_m$	: membrane surface
$_v$	: vacuum
ΔH_v	: Latent heat of vaporization (J/ kg)
A	: Membrane area (m^2)
B	: Membrane coefficient (kg /m^2 .s. Pa)
C	: Solute concentration (mol /L)
d	: Molecular diffusion coefficient (m^2/ s)
D[4, 3]	: Volume weighted mean size (μm)
d_h	: Hydraulic diameter (m)
D^{kn}	: Knudsen diffusion coefficient of solute
E_{pump}	: Pumping energy (W)
H	: Global heat transfer coefficient
T_h	: Heating temperature (ºC)
h_w	: Heat transfer coefficient (W/m^2/K)
J_w	: Water flux (L m^{-2} h^{-1} = LMH)
K	: Mass transfer coefficient (m/s)
K_m	: Thermal conductivity (W /m/ K)
L	: Length of the channel (m)
m	: Molar concentration (mol/$m^{3)}$
M	: Molecular mass of water (kg/mol)
N	: Heat flux (L m^{-2} h^{-1}/ LMH)
Nu	: Nusselt number
P	: Pressure (Pa)
P'	: Applied pressure (Pa)
P_m	: Vapour pressure on membrane surface (Pa)
P_p	: Permeate pressure (kPa)
Pr	: Prandtl numbers
Q	: Flow rate (L/h)
R	: Gas constant (J /mol/ K)
r	: Pore size (m)

Re	: Reynolds number
S	: Water-specific heat capacity (kJ/kg)
Sc	: Schmidt number
Sh	: Sherwood number
T	: Temperature (ºC)
t	: Time (min)
t_{ind}	: Induction period (min)
v	: Velocity (m/s)
δ	: Membrane thickness (m)
ε	: Porosity
ζ.	: Zeta potential (mV)
λ	: Mean free path of water molecules (m)
μ	: Viscosity (Pa s)
ρ	: Density (kg/m^3)
τ	: Tortuosity

TABLE OF CONTENTS

CERTIFICATE ii

ACKNOWLEDGEMENTS iii

JOURNAL ARTICLES PUBLISHED v

CONFERENCE PAPERS AND PRESENTATIONS vi

LIST OF ABBREVIATIONS vii

LIST OF SYMBOLS ix

TABLE OF CONTENTS xi

LIST OF FIGURES xx

LIST OF TABLES xxvii

ABSTRACT xxx

CHAPTER 1 INTRODUCTION 1

1.1 BACKGROUND OF RESEARCH 2

1.1.1 Global demand for drinking water 2

1.1.2 Fresh water for remote areas in Australia 2

1.1.3 Membrane Distillation 4

1.1.4 Industrial application of MD for drinking water 5

1.1.5 Membrane scaling and fouling phenomena in MD 7

1.2 RATIONALE OF RESEARCH 9

1.2.1 Novel modified design VMD system 9

1.2.2 Analysis of Membrane Fouling Phenomena in MD 10

1.2.3 Practical approaches for fouling mitigation in MD 11

1.3 OUTLINE (STRUCTURE) OF THIS STUDY 12

CHAPTER 2 LITERATURE REVIEW 15

2.1 INTRODUCTION 16

2.1.1 Background of MD in drinking water production 16

2.1.2 A brief history of MD applicatication for drinking water production 17

2.1.3 Advantages of MD technology for drinking water production 19

2.2 FUNDAMENTALS OF MD 22

2.2.1 MD configurations 22

2.2.2 Transfer mechanism 23

2.3 CHALLENGES OF MD TECHNOLOGY FOR DRINKING WATER PRODUCTION 28

2.3.1 Lack of commercial application 28

2.3.2 Cost and energy efficiency 29

2.3.3 Fouling development in MD related to drinking water production 29

2.4 FOULING PHENOMENA 30

2.4.1 Background of fouling 30

2.4.2 Fouling development in MD 31

2.4.3 Factors influencing organic fouling and scaling in MD 33

2.5 APPROACHES TO REDUCE FOULING IN MD 42

2.5.1 Pretreatment 42

2.5.1.1 Pretreatment in MD 43

2.5.2 Advances in technology 43

2.6 SUMMARY 44

CHAPTER 3 EXPERIMENTAL INVESTIGATIONS 46

3.1 EXPERIMENTAL MATERIALS 47

3.1.1 Membrane 47

3.1.2 Solutions 48

3.2 EXPERIMENTAL METHODS 50

3.2.1 Lab scale vacuum multi effect membrane distillation (V-MEMD) 50

3.2.2 Bench scale direct contact membrane distillation (DCMD) 55

3.3 EXPERIMENTAL ANALYSES 57

3.3.1Solution and Foulant Characteristics 57

3.3.1.1 Primary analysis 57

3.3.1.2 Inorganic analysis 57

3.3.1.3 Organic analysis 59

3.3.1.4 Biological analysis 62

3.3.2 Membrane characterization 63

3.3.2.1 Field emission scanning electron microscope (FE-SEM) 63

3.3.2.2 Contact angle measurement 64

CHAPTER 4 OPTIMAL OPERATING CONDITIONS FOR MD 66

4.1 OPERATING PARAMETERS INFLUENCING THE PERFORMANCE OF V-MEMD 68

4.1.1 INTRODUCTION 68

4.1.2 MATERIALS AND METHODS 70

4.1.2.1 Experimental Set up 70

4.1.2.2 Experimental Operating Conditions 70

4.1.2.3 Performance measurement methods 71

4.1.3 RESULTS AND DISCUSSION ON OPERATING PARAMETERS INFLUENCING THE PERFORMANCE OF THE V-MEMD SYSTEM 73

4.1.3.1Influence of feed velocity 73

4.1.3.2 Influence of feed temperature 73

4.1.3.3 Influence of permeate vacuum pressure 74

4.2 V-MEMD SALINITY EXPERIMENT AND MODELING 76

4.2.1 EXPERIMENTAL OPERATING CONDITIONS 78

4.2.2 MODELING THEORY 80

4.2.2.1 Modeling Equations 80

4.2.2.2 Estimating Feed Temperature 85

4.2.3 RESULTS AND DISCUSSION FOR THE V-MEMD SALINITY EXPERIMENT AND MODELING 87

4.2.3.1 Effect of feed water concentration 89

4.2.3.2 Effect of feed water temperature 89

4.2.3.3Effect of feed velocity 89

4.2.3.4 Model simulation 90

4.2.3.5 Polarization effect on V-MEMD system 92

4.3 DCMD PERFORMANCE WITH SUITABLE FEED/PERMEATE VELOCITY 96

4.3.1 EXPERIMENTAL OPERATING CONDITIONS 97

4.3.2 RESULTS AND DISCUSSION ON DCMD PERFORMANCE WITH SUITABLE FEED/PERMEATE VELOCITY 98

4.3.2.1 Optimal flow velocity 98

4.3.2.2 Optimal permeate flow velocity 101

4.4 SUMMARY 105

4.4.1 Summarizing the operating parameters influencing the performance of V-MEMD system 105

4.4.2 Summarizing V-MEMD salinity experiment and modeling 105

4.4.3 Summarizing DCMD operating performance with suitable feed/permeate velocity 106

CHAPTER 5 SCALING DEVELOPMENT ANALYSIS IN MD 107

5.1 SCALING DEVELOPMENT ANALYSIS IN MD 109

5.1.1 INTRODUCTION 110

5.1.2 MATERIALS AND METHODS 110

5.1.2.1 Experimental Set up 110

5.1.2.2 Feed Solution 110

5.1.2.3 Scaling Experimental Operating Condition 110

5.1.2.4 Scaling Measurement 111

5.1.3 RESULTS AND DISCUSSION FOR ANALYSIS OF SCALING DEVELOPMENT IN THE V-MEMD SYSTEM 116

5.1.3.1 CaSO4 scaling development with V-MEMD (condition I) 116

5.1.3.2 Influence of different operating conditions on CaSO4 scaling development in the V-MEMD system 122

5.2 INFLUENCE OF FEED /PERMEATE VELOCITY ON SCALING DEVELOPMENT IN A DCMD SYSTEM 130

5.2.1 EXPERIMENTAL OPERATING CONDITIONS 131

5.2.2 RESULTS AND DISCUSSION ON THE INFLUENCE OF FEED /PERMEATE VELOCITY ON SCALING DEVELOPMENT IN A DCMD SYSTEM 132

5.2.2.1 Influence of flow velocity on scaling development in DCMD 132

5.2.2.2 Influence of of permeate velocity on scaling development 140

5.3 SUMMARY 143

5.3.1 Summarizing scaling development analysis of the V-MEMD system 143

5.3.2 Summarizing the influence of feed/permeate velocity on scaling development in a DCMD 143

CHAPTER 6 ORGANIC FOULING DEVELOPMENT ANALYSIS IN MD 145

6.1 ORGANIC FOULING ANALYSIS OF THE DCMD SYSTEM 146

6.1.1 INTRODUCTION 147

6.1.2 MATERIALS AND METHODS 149

6.1.2.1 Synthetic organic compounds 149

6.1.2.2 Fouling experimental procedure 150

6.1.3 RESULTS AND DISCUSSION 153

6.1.3.1 Influence of organic compounds on fouling development in MD 153

6.1.3.2 Influence of feed solution's physico-chemical conditions on organic fouling development in MD 173

6.1.4 SUMMARY 178

6.1.4.1 Summarizing the influence of organic compounds on fouling development in MD 178

6.1.4.2 Summarizing the influence of feed solution physico-chemical conditions on fouling development in MD 179

CHAPTER 7 MD PERFORMANCE WITH PRETREATMENT AND CLEANING CYCLE 180

7.1 SUSTAINABLE PRETREATMENT PROCESSES 182

7.1.1 INTRODUCTION 182

7.1.2 MATERIALS AND METHODS 184

7.1.2.1 Materials 184

7.1.2.2 Experimental Methods 185

7.1.2.3 Experimental Analysis 188

7.1.3 RESULTS AND DISCUSSION OF PRETREATMENT EVALUATION 190

7.1.3.1 Solids removal 190

7.1.3.2 Organics removal 191

7.1.3.3 The role of bioactivity in deep-bed biofilter and SMABR 194

7.1.3.4 Biofouling potential reduction 197

7.2 MD PERFORMANCE EVALUATION 200

7.2.1 MD PERFORMANCE WITH PRETREATMENT 200

7.2.1.1 RESULTS AND DISCUSSION FOR MD PERFORMANCE WITH PRETREATMENT 201

7.2.2 MD PERFORMANCE WITH CLEANING CYCLE 208

7.2.2.1 RESULTS AND DISCUSSION OF MD PERFORMANCE WITH CLEANING CYCLE 209

7.3 SUMMARY 213

7.3.1 Summarizing pretreatment performance 213

7.3.2.1 MD performance with pretreatment 213

7.3.2.2 MD performance with membrane cleaning 214

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS **215**

8.1 CONCLUSIONS 216

8.2 RECOMMENDATIONS 223

REFERENCES **227**

LIST OF FIGURES

Figure 1.1 Arid and semi-arid areas in Australia (adopted from Australian Bureau of Meteorology, 2014). -3-

Figure 1.2 Timeline of MD application for drinking water production. -5-

Figure 1.3 Published papers on fouling analysis in MD from 1996 to 2014 (as searched through Scopus). -9-

Figure 1.4 Outline (structure) of this thesis. -13-

Figure 2.1 Schematic diagram of heat and mass transfer in MD -23-

Figure 3.1 Experimental material categories in this study. -47-

Figure 3.2 Image of the Memsys one stage V-MEMD system used in this study (A : control panel; B: heating unit; C: vacuum pump; D: distillate storage unit; E : stream raiser; F : membrane module; G : condensing system. -51-

Figure 3.3 Schematic diagram of the water flow and temperature distribution (change) ($T_1 > T_2 > T_3 > T_4$) through the one stage V-MEMD system (External temperatures from temperature sensors -T_1= steam raiser (inlet) temperature/ heating temperature, T_h; T_2=steam raiser (outlet) temperature; T_3= feed temperature (inlet)/ bulk feed temperature, T_{fb}; T_4 = feed temperature (outlet) /brine & Internal temperatures - T_f =feed temperature in membrane module; T_m = temperature on the membrane surface. -54-

Figure 3.4 Image of the DCMD experimental set-up. -56-

Figure 3.5 Schematic diagram of the DCMD experimental setup. -56-

Figure 3.6 UF-MFI experimental set-up. -59-

Figure 3.7 DOC-LABOR Liquid Chromatography-Organic Carbon Detector. -61-

Figure 4.1 Influence of feed velocity, v_f on permeate flux and recovery ratio (T_h = 65.0 °C and P_p =10.0 kPa) (L m^{-2} h^{-1} = LMH) -75-

Figure 4.2 Influence of feed temperature (represented as T_h), on permeate flux and GOR (v_f = 1.1 m/s and P_p =10.0 kPa). -75-

Figure 4.3 Influence of permeate pressure on permeate flux (v_f = 1.1 m/s and T_h =65.0 °C). -75-

Figure 4.4 The procedure (algorithm) used to calculate water flux. -86-

Figure 4.5 Permeate flux as a function of the feed concentration for different feed temperatures at v_f =1.1 m/s (Set I) (T_{fb}: ● 46.0°C; ▲ 40.5°C; ■ 37.0°C). -88-

Figure 4.6 Permeate flux as a function of the feed concentration for different feed temperatures at v_f =2.2 m/s (Set II) (T_{fb}: ○ 48.7°C; Δ 42.5°C; □ 37.0°C). -88-

Figure 4.7 Comparison between modeling and experimental permeate flux **(a)** bulk feed temperature, T_{fb}: 37.0°C, v_f: 1.1 m/s, **(b)** bulk feed temperature, T_{fb}: 37.0°C, v_f: 2.2 m/s, **(c)** bulk feed temperature, T_{fb}: 40.5°C, v_f: 1.1 m/s, **(d)** bulk feed temperature, T_{fb}: 42.5°C, v_f: 2.2 m/s, **(e)** bulk feed temperature, T_{fb}: 46.0°C, v_f: 1.1 m/s, **(f)** bulk feed temperature, T_{fb}: 48.7°C, v_f: 2.2 m/s. -91-

Figure 4.8 Polarization effect in the V-MEMD system **(a)** and **(c)** TP and CP ratio as a function of feed concentration with different feed temperatures and feed velocity (Set I and Set II) based on actual vacuum pressure value **(b)** and **(d)** TP' and CP' ratio as a function of feed concentration with different feed temperatures and feed velocity (Set I and Set II) based on reference value of 4.5 kPa vacuum pressure **(**----- 1.1 m/s; ——2.2 m/s; (I-1) 37.0ºC (I-2) 40.5ºC (I-3) 46.0ºC (II-1) 37.0ºC (II-2) 42.5ºC (II-3) 48.7ºC).

-95-

Figure 4.9 Performance output of DCMD with DI water at varied flow velocity ratio.

-100-

Figure 4.10 Permeate flux as a function of varying permeate velocity at v_f = 0.14 m/s.

-102-

Figure 4.11 Permeate flux and P'_p/P'_f as a function of varying permeate velocity at v_f = 0.8 m/s. -102-

Figure 5.1 Scaling development pattern in V-MEMD condition I (T_h=60 ˚C, P_v =10.0 kPa, v_f =0.9 m/s) represented by permeate flux, turbidity, CF and SR as a function of time. -117-

Figure 5.2 Gypsum crystal size distribution (CSD) in V-MEMD condition I **(a)** final feed solution, $CSD_{brine\ feed}$ **(b)** brine from DI water flushing, $CSD_{brine\ module}$ (*Note: average value is given from three samples)*.. -121-

Figure 5.3 Comparing V-MEMD permeate flux pattern based on varied permeate vacuum pressure - experimental conditions I to III (P_v= 10.0 kPa to 15.0 kPa) and varied feed velocity - experimental conditions I, IV and V (v_f =0.9 m/s to v_f =0.3 m/s). -123-

Figure 5.4 Crystal size distribution (CSD) with different permeate vacuum pressure, P_v=10.0 kPa to P_v=15.0 kPa at **(a)** final feed solution, $CSD_{brine\ feed}$ and **(b)** brine from DI water flushing, $CSD_{brine\ module}$. -126-

Figure 5.5 Crystal size distribution (CSD) at different feed velocities, v_f=0.9 m/s to 0.3 m/s based on (**a)** final feed solution, $CSD_{brine\ feed}$ and **(b)** brine from DI water flushing, $CSD_{brine\ module}$. -129-

Figure 5.6 DCMD scaling pattern at high flow velocity (v_f & v_p = 2.2 m/s), intermediate flow velocity (v_f & v_p = 1.1 m/s), and low flow velocity (v_f & v_p = 0.5 m/s) (feed solution = $CaSO_4$ and F_t = 70 °C). -135-

Figure 5.7 SEM – EDS images of membrane cross-section **(a)** v_f & v_p = 0.5 m/s **(b)** v_f & v_p = 1.1 m/s **(c)** v_f & v_p = 2.2 m/s **(d)** line analysis of the percentage mass of calcium and sulphur element deposit.. -137-

Figure 5.8 Scaling development at intermediate velocities (v_f & v_p =1.1 m/s) as a function of feed VCF in phase (i) - (iii) (permeate flux (──), feed turbidity (-----), feed solution $CaSO_4$ and F_t =70 ºC). Note: Adjunct points were connected in a straight line for easy reference. -139-

Figure 5.9 DCMD scaling pattern comparison at different combination settings of v_f & v_p (v_f & v_p = 0.8 m/s; v_f & v_p =1.1 m/s; v_f = 0.8 & v_p = 1.1 m/s) (feed solution $CaSO_4$ and F_t = 70 ºC). -141-

Figure 5.10 SEM –EDS images of membrane cross-section for comparison of v_p effect (a) v_f &v_p = 0.8 m/s (b) v_f = 0 .8 m/s, v_p= 1.1 m/s (c) v_f & v_p = 1.1 m/s (d) line analysis of the percentage mass of calcium and sulphur element deposit. -142-

Figure 6.1 Comparison of the permeate flux pattern of the three individual organic compound feed solutions as a function of VCF. -153-

Figure 6.2 LC-OCD chromatogram of membrane foulants of the three individual organic compound feed solutions *(A: Biopolymers; B: HS; C: BB; D: LMW organics).*

-154-

Figure 6.3 LC-OCD chromatogram of the three organic feed solutions **(a)** AA **(b)** HA and **(c)** BSA *(A: Biopolymers; B: HS; C: BB; D: LMW organics).* -163-

Figure 6.4 SEM-EDS membrane surface analysis of **(a)** virgin **(b)** HA **(c)** AA and **(d)** BSA. -167-

Figure 6.5 SEM-EDS membrane cross-section line analysis **(a)** carbon element mass as a function of membrane depth on HA, BSA and AA fouled membrane and SEM images of **(b)** virgin membrane **(c)** AA **(d)** HA and **(e)** BSA. -168-

Figure 6.6 LC-OCD chromatograms of the MO feed solution *(A: Biopolymers; B: HS; C: BB; D: LMW organics).* -172-

Figure 6.7 Comparison of fouling pattern with MO solution **(a)** permeate flux decline as a function of VCF **(b)** LC-OCD chromatogram of MO foulant *(A: Biopolymers; B: HS; C: BB; D: LMW organics).* -172-

Figure 6.8 Physico-chemical influence of fouling pattern of HA compound based on permeate flux decline, LC-OCD chromatograms of feed solution and membrane foulant (**a-c)** feed II (saline HA) **(d - f)** feed III (inorganic scalant HA compound ($CaSO_4$)) *(A: Biopolymers; B: HS; C: BB; D: LMW organics)*. -174-

Figure 7.1 Experimental set-up of GAC deep-bed biofilter. -186-

Figure 7.2 Experimental set-up of the SMABR system. -187-

Figure 7.3 LC-OCD chromatogram representing the characteristics of the organic compounds present in the seawater **(b)** LC-OCD chromatograms of GAC biofilter effluent highlighting the reduction of LMW organics at different stages *(A: Biopolymers; B: HS; C: BB; D: LMW organics).* -192-

Figure 7.4 Relationship between bacterial growth and DOC removal on the GAC biofilter at different stages. -196-

Figure 7.5 ATP concentration at different depths of media of the GAC biofilter at different stages. -196-

Figure 7.6 AOC concentration of seawater and GAC biofilter effluent at different stages. -198-

Figure 7.7 Changes in AOC concentrations of SW and effluents. -199-

Figure 7.8 DCMD fouling pattern with SW **(a)** permeate flux pattern **(b)** LC-OCD chromatogram changes of SW feed solution from VCF 1.0 to VCF 4.0 **(c)** LC-OCD chromatogram of membrane foulant at VCF 4.0 **(d)** LC-OCD chromatogram of permeate at VCF 4.0 *(A: Biopolymers; B: HS; C: BB; D: LMW organics).* -202-

Figure 7.9 Comparison of permeate flux pattern in raw and prettreated SW-70ºC operation. -204-

Figure 7.10 Comparison of fouling pattern in raw and pretreated SW-70ºC operation **(a)** initial feed solution chromatogram analysis **(b)** permeate flux pattern *(A: Biopolymers; B: HS; C: BB; D: LMW organics).* -205-

Figure 7.11 SEM-EDS membrane cross-section line analysis of virgin, SW and pretreated SW membrane. -207-

Figure 7.12 The V-MEMD performance over time with high TDS saline feed solution. -209-

Figure 8.1 Comparison of the production rate of **(a)** V-MEMD system and **(b)** small-scale RO system (data of small-scale RO system adopted from Banat et al., 2012). -218-

Figure 8.2 Schematic diagram of MD design concept for drinking water production in inland area. -224-

LIST OF TABLES

Table 2.1 Advantages of MD technology. -20-

Table 2.2 MD configuration description. -22-

Table 2.3 Polarization reduction strategy with different operational settings. -28-

Table 2.4 Description of fouling categories. -31-

Table 2.5 Influence of feed temperature on scaling development in MD. -39-

Table 2.6 Summary on the research gaps in MD studies. -45-

Table 3.1 Characteristics of membrane used in this study. - 47-

Table 3.2 Inorganic chemical solutions used in this study. -48-

Table 3.3 Organic chemical solutions used in this study. -49-

Table 3.4 Characteristics of seawater in Chowder Bay in Sydney, Australia. -49-

Table 3.5 Summary of experimental analyses used in this study. -65-

Table 4.1 V-MEMD operating parameter setting for salinity study. -79-

Table 4.2 Influence of different operating conditions on the ratio of TP' and CP'. -94-

Table 4.3 Influence of P'_p/P'_f and cooling temperature gradient on permeate flux based on varying v_p/v_f (v_f = 0.8 m/s). -101-

Table 4.4 Comparisons of DCMD performance at different combination settings of v_f & v_p. -104-

Table 5.1 Experimental feed solutions. -110-

Table 5.2 Scaling experimental setting at a constant heating T_h= 60ºC. -111-

Table 5.3 Summary of experimental results with varied permeate vacuum pressure (T_h= 60 ºC, v_f =0.9 m/s). -124-

Table 5.4 Summary of scaling analysis at high, intermediate and low flow velocity settings. -133-

Table 5.5 Comparisons of DCMD performance at different v_f & v_p combination settings. -140-

Table 6.1 Synthetic organic compound feed solution composition, representation and operating conditions. -151-

Table 6.2 Detailed characteristics of the individual organic feed solutions -156-

Table 6.3 LC-OCD organic analysis details of the glassware test showing the effect of heating on HA compound. -160-

Table 6.4 LC-OCD organic characteristics of HA compound at different feed temperatures (F_t = 50ºC, F_t = 60ºC and F_t = 70ºC) with DCMD operation. -161-

Table 6.5 LC-OCD organic characteristics details of the permeate solution at VCF 4.0. -164-

Table 6.6 HA organics fouling pattern under MD operation with different physico-chemical conditions (HA feed I to feed III). -177-

Table 7.1 Organic fraction of seawater (SW) and SMABR effluent for a duration of 47 days (Unit: mg/L). -194-

Table 7.2 The DOC characteristics of feed and permeate of the raw SW and pretreated SW. -207-

Table 7.3 Mass balance of the components in feed II from the initial feed solution concentration factor (CF 1.0) to the final feed solution concentration factor (CF 3.3). -210-

Table 7.4 Recovery of components in feed II with DI water flushing. -211-

ABSTRACT

Around 40% of the world's population lives in arid and semi-arid regions where rainfall is low. These regions are facing challenges of declining water tables and increasing ground water salinity. Providing good quality drinking water for small communities in these areas is highly challenging. Although existing membrane technologies are able to produce potable quality water, issues such as high energy consumption, osmotic pressure constraint, brine management and large centralized designs make them unsuitable for application in these areas. Membrane distillation (MD), a thermal integrated membrane process, is a burgeoning technology with the potential to address and overcome these issues. As a vapour pressure operated system, MD is not restricted by saline feed solutions and therefore can achieve good quality distillate with minimal brine discharge. Furthermore, an MD system can be built as a standalone compact system suitable for small community application. The modest temperature requirement for MD operation (generally between 60ºC to 80ºC) enables the system to use alternative energy sources such as solar power. Despite such advantages, MD has not as yet been used widely in commercial applications. Several essential problems concerning MD process performance, namely, lower production rate, fouling propensity, energy efficiency and long term performance must be addressed.

In this study, the performance of a scaled-up modified design vacuum membrane distillation system termed 'vacuum multi effect membrane distillation (V-MEMD)' was evaluated. A bench scale direct contact membrane distillation (DCMD) was employed for detailed fouling analysis. The four main sections of this work incorporate: (i) V-MEMD operation; (ii) scaling development in MD; (iii) organic fouling development in MD; and (iv) pretreatment and membrane cleaning in MD. These sections present and explain critical aspects of MD performance in the context of drinking water production.

V-MEMD operation Firstly, in this study the beneficial features of a modified V-MEMD system were highlighted. These include the internal heating and internal condensing which reduces heat loss and makes operation possible at modest feed temperatures from 45ºC to 55ºC. A semi-empirical mathematical modeling in this study showed that operating at these feed temperature ranges minimized the effect of temperature polarization (TP) to a low range of between 0.96 and 0.99. The findings of the V-MEMD performance analysis indicated that feed temperature and permeate pressure were the most influential operating parameters. Lowering the permeate pressure from P_p =15.0 kPa to 10.0 kPa increased the permeate flux by almost 200%, whereby the highest permeate flux of 13.5 L m^{-2} h^{-1} (LMH) was achieved when the permeate pressure was reduced to P_p =5.0 kPa. In the V-MEMD concept, vacuum application is essential in order to create a sustainable driving force, especially for a scaled up modular unit with several membrane stages. At the same time, increased feed temperature exponentially increased the permeate flux. A small variation of feed temperature from 45.0°C to 65.0°C significantly improved the permeate flux from 3.6 LMH to 11.8 LMH.

The V-MEMD system proved to be suitable for producing 9.4 LMH of good quality permeate (more than 99.5% rejection rate) with highly saline feed water (1 M of NaCl feed solution concentrated up to 3 M of NaCl). Only a 10-15% reduction in permeate flux was observed at high feed concentration. The modeling data revealed that high turbulent feed flow velocity of 2.2 m/s (Re = 17, 300) in the V-MEMD system effectively minimized concentration polarization (CP), but the recovery ratio reduced with increased feed flow velocity. An intermediate feed flow velocity of 1.1 m/s (Re = 6,100) was more appropriate for balancing the effect of CP and maintaining a reasonable recovery ratio.

Scaling development in MD In achieving near zero liquid discharge under thermal conditions, inevitably, the MD membrane would be exposed to highly concentrated sparingly soluble salts such as calcium sulphate ($CaSO_4$). In this study, an evaluation of $CaSO_4$ scaling development in MD operation was carried out, focusing on the role of hydrodynamic (flow velocity) conditions. This study found that permeate condition influenced $CaSO_4$ scaling development. For instance, in the V-MEMD system, the $CaSO_4$ crystal size in the membrane module increased from 62.68 μm to 522.28 μm, with increased permeate pressure from 10.0 kPa to 15.0 kPa. Similarly, in a DCMD configuration, a small change in the permeate velocity from 0.8 m/s to 1.1 m/s was effective in changing the scaling pattern from surface crystallization to a more dominant bulk crystallization, without the need to change the feed velocity while improving the system's performance (i.e. increase recovery ratio, reduce pumping energy, increase permeate flux). Importantly, the findings of this study also revealed that the crystals were only loosely deposited on the membrane.

In the V-MEMD system, the loose deposition was attributed to the lack of hydraulic pressure, low feed temperature (T_f = 47.6 °C), high turbulence (Re = 5665.6, 0.9 m/s) and short membrane retention time (21.6 s). Increasing the feed flow velocity from 0.3 m/s to 0.9 m/s in the V-MEMD reduced the gypsum crystal size in the membrane module from 339.03 μm to 62.68 μm. Likewise, in the DCMD configuration the high feed velocity (turbulence) played an important role in controlling the membrane surface crystallization. The Field Emission Scanning Electron Microscope (FE-SEM) analysis with EDS showed significantly higher calcium and sulphate element deposition on the membrane at low feed velocity (0.5 m/s) compared to the high flow velocity (2.2 m/s).

Organic fouling development in MD Organic fouling is a ubiquitous problem in membrane processes. Compared to pressure driven membrane processes, the fouling

phenomenon in MD operation is unique due to the presence of thermal conditions on a hydrophobic membrane at supersaturated feed concentration levels. In depth understanding of the MD fouling phenomenon is crucial if MD is to be successfully implemented in a proto-scale. This research carried out a detailed fouling development analysis using Liquid Chromatography-Organic Carbon Detection (LC-OCD) to characterize the behavior of organic compounds under thermal MD operation. The findings of this research established that organic fouling in MD was influenced by the type of organic compound present in the feed solution, the thermal state as well as the physico-chemical condition of the feed solution. Based on the LC-OCD analysis of the feed and permeate solution and membrane foulant as well as membrane analysis (contact angle and SEM-EDS analysis), both the humic acid (HA) and bovine serum albumin (BSA) compounds showed dominant fouling tendencies while the alginic acid (AA) compound exhibited minimal fouling tendencies. The latter was due to its hydrophilic nature and negative electrostatic repulsion.

The membrane SEM-EDS analysis showed that mainly the BSA compound was deposited on the membrane surface (800.6 mg/m^2 organic mass per membrane area) compared to the HA compound (423.2 mg/m^2). This was due to the hydrophobic nature of the BSA compound which allowed it to bond with the hydrophobic MD membrane. Meanwhile, the humic substances (HS) showed changes under MD thermal conditions. The LC-OCD analysis of the HA feed solution revealed the thermal disaggregation of the HS, forming low molecular weight–HS (LMW-HS) organics. Further, the cross-section membrane SEM-EDS line analysis showed the penetration of the LMW-HS organics through the membrane pores, resulting in partial wetting. The findings for the influence of physico-chemical state of the feed solution revealed that the addition of salinity (NaCl) contributed to higher HS disaggregation to LMW-HS organics. This

resulted in severe penetration of the LMW-HS organics to the permeate side. Meanwhile, in the presence of inorganics Ca^{2+} ion that acts as a binding agent, a cake layer was formed on the membrane.

Pretreatment and membrane cleaning in MD Finally, a practical application of MD was presented in this study by analysing the pretreatment and membrane cleaning in MD. In the first part of this section, the performance of two chemical-free pretreatments (namely, deep-bed biofilter and a submerged membrane adsorption bioreactor system (SMABR) was evaluated in terms of organic fouling reduction. Both these pretreatment systems helped to reduce HS and LMW organics as well as assimilable organic carbon (AOC) concentrations through adsorption and biodegradation mechanisms. In the second part of this section, MD performance with natural seawater was compared to SMABR pre-treated seawater. The natural seawater, which predominantly contains HS, resulted in the formation of LMW-HS organics under MD thermal conditions and pore penetration was observed to occur through the membrane.

The biofouling potential of MD operation with SW was highlighted based on the AOC concentration of the membrane foulant and feed solution. In the meantime the SMABR pre-treated seawater feed solution containing low concentrations of HS and LMW organics, resulted in more stable permeate flux and minimal LMW-HS organics pore penetration. The findings established the suitability of chemical-free pretreatments to reduce organic fouling in MD. Additionally, the membrane cleaning by water was carried out to flush away the loose deposition of crystals in the V-MEMD system. Based on the feed solution ion mass balance, with only 2 L of DI water, most ions in the feed solution, specifically the Mg, Na and Cl ions, were removed. This finding established the effectiveness of frequent DI water flushing for the V-MEMD system